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High-temperature solid-oxide fuel cells New trends in materials research

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The paper is an overview of basic solid-oxide fuel cells (SOFC) components in terms of their fundamental functional parameters such as chemical stability, transport as well as catalytic and thermomechanical properties under, operational conditions in a fuel cell. An interrelation between the defect structure of these materials related to oxygen nonstoichiometry and their electronic properties and catalytic activity is shown. A single-chamber fuel cell concept is also presented.

Key words: *solid-oxide fuel cell; SOFC; electrode material; electrolyte*

1. Introduction

Recently observed great interest in fuel cell technology is due to the possibility of directly converting energy stored in hydrogen-containing fuels into electrical energy. A relatively simple construction of such a device and a high efficiency of electricity generation, noise-free operation due to the lack of mobile parts, and low level of waste products make this technology the most prospective for future electrical energy sources. The rate of “charging” (fuel refill) and potential reversibility of this process (storage of instantaneous energy excess in the form of chemical energy) are additional benefits. In the large group of fuel cells special attention has been paid to solid -oxide fuel cells (SOFC) [1–4]. Their commercial importance is connected to the construction of stationary generators with powers of at least 1 MW.

A wide application of this technology is hindered by some properties of the electrode materials and of the electrolyte, as well as high-temperature reaction conditions. The presently used yttrium-stabilized zirconia (YSZ), with low ionic conductivity, must operate at about 1000 °C. This implies a short service life of the cell (thermal

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degradation of materials) and requires expensive and toxic materials, like $LaCrO_3$, for interconnectors, which raises problems for miniaturization and safety and increases costs. Lowering the service temperature to 600 °C is considered a strategic goal for the technological development of SOFCs, and calls for application of a suitable solid electrolyte, which at that temperature would have a purely ionic conductivity of 10^{-2} $S\cdot cm^{-1}$ and would be stable within the oxygen pressure range $1–10^{-20}$ atm.

2. Electrical, catalytic and thermomechanical properties of materials used in SOFCs

Figure 1 schematically illustrates the structure and functions of the SOFC components. Different aspects can be considered in the functioning of each component, e.g. transport and catalytic properties or structural and thermomechanical properties.

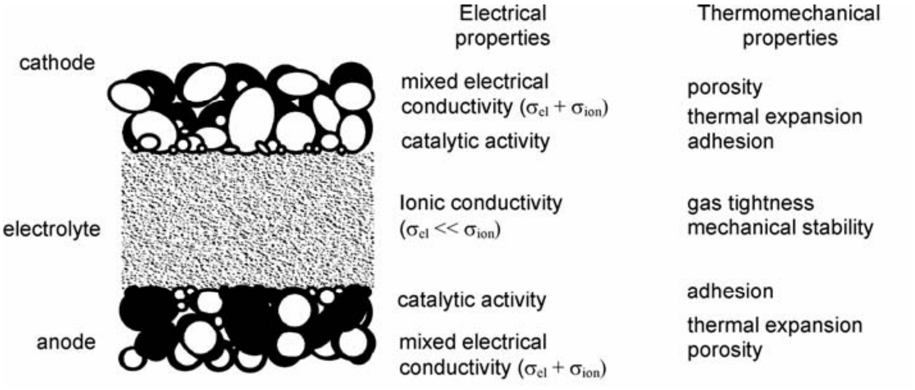

Fig. 1. Schematic cross-section of a SOFC;
structure, properties, and functions of SOFC components

2.1. Transport and catalytic properties

The cathode made of $LnMeO_3$-type oxides (Me = Mn, Fe, Co, Ni) with a perovskite structure is a mixed ionic-electronic conductor. The ionic conductivity is related to oxygen nonstoichiometry (oxygen vacancies), while the electronic conductivity to the mixed valency of cations, Me^{3+}/Me^{4+}, depending on the extent of oxygen nonstoichiometry and the amount and type of dopants. The cathode material plays the role of a catalyst for the reduction of oxygen. Since it operates in air or oxygen, the stability of oxides is not a problem.

The solid electrolyte (YSZ, CeO_2 (Gd, Sm)), as a purely ionic conductor with oxygen vacancies as carriers, is stable over a wide range of oxygen pressures ($1–10^{-20}$ atm); near the cathode it operates in highly oxidizing conditions and near the anode (fuel supply) in highly reducing ones. The ionic conductivity at the service temperature should be about 10^{-2} S·cm^{-1}. So far, no real system has been found to satisfy both mentioned requirements.

The anode (Ni/YSZ or Ni/CeO_2(Gd, Sm) cermet) is an ionic-electronic conductor. Its ionic conductivity is related to oxygen vacancies in YSZ or in CeO_2 (Gd, Sm). The electronic conductivity results from the existence of a conductive percolation path at 30% Ni concentration in the anode material. Nickel catalyses the fuel oxidation. Highly reducing atmosphere is not detrimental for the anode material, furthermore it improves its effectiveness (maintains the catalytic activity of nickel and raises the electrical conductivity of CeO_2).

2.2. Structural and thermomechanical properties

The cathode and anode materials should be porous, in order to allow the penetration of gases. In the layers close to the electrolyte, however, the porosity should be as low as possible to intensify the lattice diffusion of oxygen. The electrolyte is a gas-tight sinter with high strength, preventing a non-productive combustion of the fuel. All the cell components should be chemically and thermally compatible.

3. Electrolytes in intermediate temperature SOFCs (IT-SOFCs)

It seems that some improvements of the properties of solid electrolytes based on ZrO_2 are still technologically feasible. This especially refers to electrical conductivity which might be increased by doping. It has been shown [5] that scandium dopant in zirconia can raise conductivity by two orders of magnitude but its scarce occurrence in the earth crust and high price excludes this element from practical applications. Another possibility for improving the electrical conductivity of zirconia-based electrolytes is to develop the technology of thicker than 1 mm, gas-tight YSZ layers, and to modify the microstructure of zirconia (nanocrystalline layers, a dispersed composite Y_2O_3–ZrO_2–Al_2O_3 electrolyte [6, 7]). Electrolytes based on bismuth oxide, Bi_2O_3, exhibit high ionic conductivity but Bi_2O_3 undergoes reduction to metallic bismuth at low oxygen pressures. Some oxides with the perovskite structure (e.g. $SrCe_{0.95}Yb_{0.05}O_{3-y}$, $CaZr_{0.96}Y_{0.04}O_{3-y}$ [8]), showing proton conductivity, have also been investigated.

From among the many oxide conductors studied, cerium dioxide (CeO_2), stabilized with rare-earth oxides (i.e. with samarium or gadolinium) is most often quoted as a candidate for IT-SOFC. This electrolyte has an electrical conductivity higher than the ZrO_2-based electrolytes and lower activation energy of conductivity. Solid electrolytes $Ce_{0.8}Sm_{0.2}O_2$ (referred to as SDC) and $Ce_{0.9}Gd_{0.1}O_2$ (GDC) have, so far, the highest oxide-ion conductivity, reaching about 10^{-1} S·cm^{-1} at 800 °C [9]. An important benefit of CeO_2-based electrolytes compared to ZrO_2 is their chemical and thermal compatibility with the new generation of cathode materials, $LaMO_3$ (M = Mn, Co, Fe, Ni), with a perovskite structure and the thermal expansion coefficient very close to that of interconnectors made of high-chromium ferritic steels. The most troublesome deficiency of electrolytes based on CeO_2 in commercial use is that its oxygen nonstoichiometry increases at high temperatures and low oxygen pressures, $pO_2 < 10^{-14}$ atm (reducing conditions near the anode), which gives rise to an undesirable electronic conduction related to the following reaction:

$$\mathrm{O_O^x} = \mathrm{V_O^{\bullet\bullet}} + 1/2\,\mathrm{O_2} + 2\mathrm{e^-} \tag{1}$$

The elimination of electronic conduction and widening of the oxygen pressure range to 10^{-20} atm, where the transport number of oxygen ions equals 1, remains one of the essential problems to be solved. This can be done by doping of the cerium sublattice with selected ions with valencies different from that of cerium. A challenging task for solid-state chemistry is to assess the interrelations between the types of point defects connected with oxygen nonstoichiometry and foreign dopant atoms, their concentrations, crystal structures, and transport properties.

4. Cathode materials in IT-SOFC

Cathode materials in IT-SOFC must satisfy the following requirements: mixed ionic-electronic conductivity, thermal and chemical stability at high temperatures in air and good chemical and thermo-mechanical compatibility with the electrolyte. The cathode material also plays the role of a catalyst in the reduction of oxygen:

$$1/2\,\mathrm{O_2} + \mathrm{V_O^{\bullet\bullet}} + 2\mathrm{e^-} = \mathrm{O_O^x} \tag{2}$$

Mixed ionic-electronic conductivity and a significant open porosity enable oxygen reduction not only on the surface but also in the entire volume of the electrode.

Candidate materials for cathodes in IT-SOFCs are searched for in two groups of compounds with perovskite structures: $Ln_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (where: Ln = La, Sm, Nd, Gd, Dy) – referred to as LSCF – and $Ln_{1-x}A_xM_{1-y}Mn_yO_{3-\delta}$ (where: Ln = La, Nd, Pr; A = Ca, Sr; M = 3d metal other than manganese) [10, 11]. Recently, compounds such as $(La,Sr)Ni_{1-y}Fe_yO_3$ [12] and $LaNi_{1-y}Co_yO_3$ [13] have also been under investigation.

The basic problem concerning $LaMO_3$ (M = Mn, Fe, Co, Ni) cathode materials is their insufficient rate of oxygen-ion transport at 600 °C. Moreover, depending on oxygen partial pressure, the type of dominating defects may change from oxygen excess ($LaMO_{3+y}$) to oxygen deficiency ($LaMO_{3-y}$). For the cathode material, the most advantageous defects are oxygen vacancies. These defects are often formed at oxygen partial pressures $pO_2 < 10^{-3}$–10^{-4} atm, while the cathode operates in air. One of the important research tasks is to shift the stability range of oxygen vacancies to higher oxygen pressures (0.21 atm). It has been reported [4] that strontium-doped (50%) $La_{1-x}Sr_xMnO_3$ changes the conduction mechanism at high temperatures from a small polaron mechanism to metallic conduction, which is a very desirable behaviour in

SOFCs. Metallic conduction can also be obtained in the group of oxides with the formulas $La_{1-x}Sr_xCoO_3$ and $La_{1-x}Sr_xFeO_3$ [14].

Recently, oxides with the perovskite structure have been the subject of extensive studies [15, 16] but most research activities concentrate on their useful properties, i.e. possible applications as cathodes in SOFC. Fundamental studies, which might contribute to better understanding the relations between crystallographic structure, ionic and electronic defects resulting from nonstoichiometry, doping level, electronic structure, and transport properties or the reactivity of perovskite oxides versus oxygen are lacking. These issues are still of great importance. It has been found [4] that the kinetics of the cathode oxygen reduction may restrict the electrochemical effectiveness of SOFC. The catalytic reduction of oxygen on perovskites has not yet been sufficiently clarified. It is known that the rate of oxygen absorption by the cathode material depends on the concentrations of both oxygen vacancies and quasi-free electrons in the cathode material. Oxygen vacancies are donor centres providing quasi-free electrons on ionisation. Therefore, oxygen nonstoichiometry and foreign dopants affect the location of the Fermi level in the cathode material [17] which – according to Volkenstein's theory – controls the catalytic activity of the cathode material. The extent of oxygen nonstoichiometry (dependent on the synthesis conditions, i.e. temperature and oxygen pressure) as well as the type and concentration of dopants (which also affect oxygen nonstoichiometry) [18, 19] can control the Fermi level position and catalytic activity of the cathode material.

5. Anode materials in IT-SOFC

Anode material in high-temperature SOFCs is Ni/YSZ cermet, whereas in IT-SOFCs it is Ni/CeO_2 (Sm, Gd) [20]. The anode material, similarly as the cathode material, should be an ionic-electronic conductor. Its ionic conductivity is associated with oxygen ion transport via oxygen vacancies in YSZ or in CeO_2 (Sm, Gd). Electronic conductivity originates from the presence of metallic nickel in the anode material. For a nickel concentration of 30%, a percolation path is formed manifesting itself in macroscopic metallic properties of the anode material. Metallic nickel additionally plays the role of a catalyst in the oxidation of fuel.

Investigations of the Ni/YSZ system under operating conditions of the cell [21] indicate that the optimisation of its microstructure is necessary. Current flow brings about nickel agglomeration in the anode/electrode system, which lowers the electrochemical efficiency of the anode to a significant extent.

6. Single-chamber cell concept

The concept of a single-chamber cell, a new and very promising one, put forward by Hibino [22–24], overcomes many difficult problems unresolved so far. In this cell, the cathode and anode, both with selective electrocatalytic properties for oxygen and hydrogen, respectively, are mounted in a common space filled with a mixture of fuel and oxidant. The electrocatalytic properties of the anode in this system must be sufficient to eliminate the need for preliminary conversion of the natural fuel. The ionic current in the cell depends on the difference between the catalytic activities of the electrodes. It becomes pointless to separate the gases around the anode and cathode (simple battery design). The electrolyte can be porous and permeable to gases, which eliminates the technological difficulties connected with manufacturing thin plates of ceramic electrolytes with high strengths. As the oxygen pressure in the reaction chamber of this cell is relatively high (fuel/air mixture) compared to the oxygen pressure in the anode space of the classical cell, the instability of some oxide electrolytes, which have competitively high electrical conductivities (e.g. bismuth oxide), is no more a problem. The optimum operating temperature of a single-chamber cell is 600 ºC, for higher temperatures both electrodes catalyse the non-productive combustion of the fuel. It should be stressed that the materials selected earlier for characterization and application in classical IT–SOFCs, electrolytes (based on CeO_2) and electrode materials (cathodes based on the perovskite-type oxides $LnMO_3$ (M = Mn, Fe, Co, Ni) and anodes of Ni/CeO_2(Gd) cermet), are also suitable for single-chamber cells. In the development of materials for single-chamber cells, special attention should be paid to the catalytic selectivity and activity of both electrodes.

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